

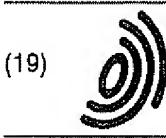
Fluoropolymer compositions containing inorganic nanometric particles

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Abstract of EP 1384750 (A1)

A polymeric composition comprising: a) from 90 to 99.9% by weight of a continuous fluoropolymer matrix; and homogeneously dispersed b) from 0.1 to 10% by weight of lamellar inorganic particles having at least one dimension lower than 100 nm having improved elastic modulus and "storage modulus" G' at high temperatures

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(54) Fluoropolymer compositions containing inorganic nanometric particles

(57) A polymeric composition comprising:

having improved elastic modulus and "storage modulus" G' at high temperatures

- from 90 to 99.9% by weight of a continuous fluoropolymer matrix; and homogeneously dispersed
- from 0.1 to 10% by weight of lamellar inorganic particles having at least one dimension lower than 100 nm

Description

[0001] The present invention relates to fluoropolymers having improved elastic modulus, "storage modulus" G' and yield stress at room temperature and even at high temperatures, higher than 100°C, maintaining the good chemical and thermal resistance properties typical of fluoropolymers

[0002] In the case of thermoprocessable fluoropolymers the addition of reinforcing fillers does not bring any substantial improvement of the polymer tensile properties (see the comparative Examples)

[0003] Thermoplastic fluorinated polymers having improved elastic modulus at room temperature containing lamellar silicate particles having nanometric sizes, are known from USP 5,962,553. Said polymers are obtained by adding thereto various types of layered silicates modified with intercalating compounds that allow their exfoliation into lamellar particles having a nanometric thickness. Said intercalating compounds are organophosphonium compounds capable to substitute the Na cations of the silicate leading to a modified layered silicate. Said modified silicate in powder form is mixed with the fluoropolymer in powder and the mixture is melted under mechanical stress, obtaining the exfoliation of the modified silicate inside the fluoropolymer matrix. However the above process shows the drawback of requiring the presence of high amounts of organic intercalating compounds in the fluoropolymer, causing a reduced chemical and/or thermal resistance thereof

[0004] The need was felt to have available fluoropolymers having improved elastic modulus, "storage modulus" G' and yield stress at room temperature and especially at high temperatures, higher than 100°C, contemporaneously maintaining the good chemical and thermal resistance properties of fluoropolymers

[0005] The Applicant has unexpectedly and surprisingly found that it is possible to prepare fluoropolymers having the above properties

[0006] An object of the present invention is a polymeric composition comprising:

- a) from 90 to 99.9% by weight of a fluoropolymer; and homogeneously dispersed,
- b) from 0.1 to 10% by weight of lamellar inorganic particles having at least one dimension lower than 100 nm

[0007] In particular b) is formed by lamellar particles having a thickness lower than 100 nm, preferably lower than 50, more preferably lower than 10, and the other two dimensions lower than 10,000 nm, preferably lower than 2,000, more preferably lower than 500 nm

[0008] As fluoropolymers a) it can be mentioned, for example:

- 1) tetrafluoroethylene homopolymer (PTFE), or tetrafluoroethylene (TFE) copolymers with less than 0.5% by moles of other fluorinated monomers, for example perfluoroalkylvinylethers (PAVE), perfluorodioxoles;
- 2) semicrystalline thermoplastic TFE copolymers with amounts higher than or equal to 0.5% by moles of fluorinated monomers, such for example perfluoroalkylvinylethers (PAVE), perfluorodioxoles, fluorosulphonyl(per)fluoroalkyl vinylether, hexafluoropropene (HFP);
- 3) chlorotrifluoroethylene homopolymer (PCTFE) and semicrystalline thermoplastic copolymers of chlorotrifluoroethylene (CTFE) with amounts in the range 0.1-5% by moles of fluorinated monomers, such for example PAVE, perfluorodioxoles, or with acrylic monomers described in USP 6,392,569;
- 4) semicrystalline thermoplastic copolymers of ethylene (E) with CTFE and/or TFE, optionally containing one or more fluorinated monomers such for example PAVE, perfluorodioxoles, or acrylic monomers described in USP 6,107,393;
- 5) polyvinylidenefluoride (PVDF) or semicrystalline thermoplastic copolymers of vinylidenefluoride (VDF) containing between 0.1% and 10% of one or more fluorinated monomers, such for example HFP, TFE, CTFE, trifluoroethylene, PAVE and perfluorodioxoles;
- 6) elastomeric VDF copolymers with one or more fluorinated monomers, as HFP, TFE, optionally containing olefinic monomers as ethylene (E), propylene, PAVE, or "cure-site" monomers containing bromine or iodine atoms;
- 7) elastomeric TFE copolymers with perfluoroalkylvinylether or perfluoroxyalkylvinylether, optionally containing ethylene (E) or propylene and "cure-site" monomers containing bromine or iodine atoms

[0009] The fluoropolymer a) is preferably a semicrystalline fluoropolymer having a second melting temperature lower than 310°C, more preferably selected in classes 3) and 4)

[0010] The lamellar inorganic particles b) are preferably formed by silicates, more preferably aluminum-silicates and/or magnesium-silicates containing other metals such as sodium, potassium, iron or lithium. As inorganic precursor of particle b) having a layered lamellar morphology can be mentioned: smectic clays formed by silicates, more preferably aluminum-silicates and/or magnesium-silicates containing other metals such as sodium, potassium, iron or lithium. Examples of smectic clays are natural minerals called montmorillonite, sausonite, vermiculite, hectorite, saponite, nontronite, or synthetic clays, for example, fluorohectorite, faponite (magnesium-silicate)

[0011] Preferably the lamellar inorganic particles b) have at least one dimension lower than 50 nm, more preferably lower than 10 nm
 [0012] The polymeric composition preferably contains from 0.3 to 6% by weight of said lamellar inorganic particles b)
 [0013] A further object of the invention is the process for obtaining the above composition, comprising:

5 1) preparation of an aqueous fluoropolymer latex having a concentration between 5 and 60% by weight, preferably between 15 and 30% by weight of fluoropolymer;
 10 2) preparation of an aqueous dispersion of lamellar inorganic particles having a thickness lower than 100 nm, preferably lower than 50 nm, more preferably lower than 10, and the other two dimensions lower than 10,000 nm, preferably lower than 2,000, more preferably lower than 500 nm, by mixing the inorganic component having a layered lamellar morphology with water until obtaining a concentration comprised between 0.1 and 10% by weight, preferably between 0.5 and 2%, under stirring (a strong mechanical stirring and/or an ultrasound treatment), at a temperature in the range 20°C-300°C, preferably 50°C-100°C;
 15 3) mixing under stirring the latex obtained in 1) with the aqueous dispersion obtained in 2);
 4) precipitation of the solid phase from the aqueous mixture obtained in 3) by cooling at temperatures lower than 0°C or by increasing the ionic strength or by pH variations;
 5) separation and drying at temperatures from 50°C to 250°C of the solid phase obtained in 4)

[0014] In step 2) the stirring is preferably a strong mechanical stirring and/or an ultrasound treatment
 20 [0015] The latex 1) is prepared by aqueous emulsion polymerization of fluorinated monomers, preferably in the presence of a surfactant or of an aqueous microemulsion based on (per)fluoropolyethers
 [0016] When the concentration of the latex prepared in 1) is lower than 30% it is possible to directly add to said latex the inorganic component having a layered lamellar morphology, thus avoiding step 2)
 25 [0017] With "microemulsion" it is meant a thermodynamically stable oil/water (O/W) system formed by a mixture of water, a fluorinated surfactant and an oil phase based on (per)fluoropolyether, which appears as a clear solution. See for example USP 4,864,006, USP 5,498,680, USP 5,959,026 and USP 6,103,843
 [0018] The latex fluoropolymer particles have dimensions comprised between 20 and 300 nm, preferably between 50 and 150 nm. Said latexes are obtained by controlling the surfactant amount used in the polymerization and/or the monomer conversion. For example, at equal conversion, by reducing the surfactant, latex particles having larger dimensions are obtained; at equal surfactant content, a conversion decrease leads to a reduction of the particle size of the latex
 30 [0019] As inorganic components having a layered lamellar morphology are used those previously defined
 [0020] The invention process leads to a fluoropolymer powder in which the lamellar inorganic particles are homogeneously dispersed
 35 [0021] Therefore the invention powders are obtainable by mixing a fluoropolymer latex with an aqueous dispersion of the lamellar inorganic component (step 2), and then by carrying out the further process steps. In process step 2) the inorganic particles are exfoliated as it can be seen by the AFM analysis (see the characterization method of the Examples). The thickness can reach the monolamellar level or there can be overlapping of some lamellas. By AFM analysis thicknesses from 1 to 2 nm are noticed. The largest particle dimension is about 400 nm for the montmorillonite and about 50 nm for the laponite. By AFM analysis the skilled man in the art is able to determine the inorganic particle dimensions
 40 [0022] The invention composition powders can be compression moulded or extruded to give shaped articles as sheets, pipes, films
 [0023] A further object of the present invention is an aqueous mixture comprising from 5% to 90% by weight of:
 45 I) fluoropolymer a) particles having dimensions in the range 20-300 nm; and
 II) lamellar inorganic particles b) having at least one dimension lower than 100 nm,

50 wherein the ratio by weight between the fluoropolymer and the lamellar inorganic component is in the range 1-1,000. For example said mixture may contain from 0.1 to 10% by weight of inorganic particles II) referred to the sum I)+II)
 [0024] Said aqueous mixture is obtainable according to the sequence of steps 1), 2) and 3) of the invention process. Said aqueous mixture can be used to obtain a continuous and homogeneous polymeric film or coatings by water evaporation
 [0025] Some Examples follow for illustrative purposes and are not limitative of the present invention.

EXAMPLES

[0026] The following characterizations carried out on the components of the Examples are hereinafter listed:

- Melt Flow Index (M.I.)

[0027] The M I of the fluorinated polymers is measured according to the ASTM D 1238 method;

5 - Second melting temperature (T_{mII}) and crystallization temperature (T_{xx})

[0028] The T_{mII} and the T_{xx} of the fluorinated polymers are determined by differential scanning calorimetry (DSC);

10 - Dynamic-mechanical measurements (DMS)

[0029] They have been carried out according to the ASTM D 4065 method by using a Rheometric ARES dynamic-mechanical spectrometer having a Temperature ramp of about +2°C/min and a constant frequency equal to 6.28 rad/sec. With said measurement the "Storage Modulus" G' is obtained in function of the temperature;

15 - Mechanical properties

[0030] At 23°C and at 100°C according to the ASTM D 1708 method, on compression moulded plaques;

20 - DLLS (Dynamic Laser Light Scattering)

[0031] The polymer latex particle diameter values have been obtained according to the Photon Correlation Spectroscopy technique, or so called Dynamic light scattering (B. Chu, "Laser Light Scattering", Academic Press, New York, 1974), by an instrument produced by Brookhaven Scientific Instrument and composed by the BI9000 correlator and by the BI200SM goniometer. The used light source is an argon ion laser Spectra Physics (wave length 514.5 nm)

25 - Optical microscope

[0032] The optical microscopy analyses have been carried out with a Zeiss microscope

30 - X-ray

[0033] The low angle X ray scattering measurements have been obtained by a Kratky chamber, by using the copper K α radiation (1.54 Angstrom). The intensity data have been collected by a positional detector Mbraun OED-50M in the angular range 0.1-5° (2θ)

35 - Atomic Force Microscopy (AFM-Atomic Force Microscopy)

[0034] The analyses have been carried out by a Park Autoprobe microscope in a No Contact mode on a layer obtained by the lamellar inorganic component dispersion diluted in water to 0.1% by weight concentration, deposited on mica and dried.

40 - Granulometry

[0035] The granulometry measurements of the inorganic component have been carried out by riddling the powder through Endecotts sieves having different mesh sizes, comprised between 600 and 75 micron, subjecting the powder to mechanical vibration (frequency 7) for 10 minutes

EXAMPLES

50 - EXAMPLE 1

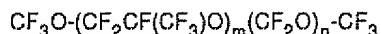
A) Polychlorotrifluoroethylene (PCTFE) latex

[0036] A PCTFE homopolymer latex has been prepared according to patent EPA 1,067,146

55 [0037] In an enamelled autoclave equipped with enamelled baffles and stirrer working at 300 rpm there were introduced in sequence:

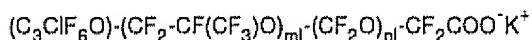
- 8.2 l of demineralized water;

- 112.5 g of a microemulsion formed by: 20% by weight of Galden® D02, having formula:



5

having m/n = 20 and average molecular weight of 450; 40% by weight of a surfactant having formula:



10

having m1/n1 82.7 and average molecular weight of 527; and 40% by weight of demineralized water;

- 4 kg of chlorotrifluoroethylene.

[0038] Then the autoclave was heated to the reaction temperature of 60°C and the radical initiator under the form of a solution of 19 g of potassium persulphate dissolved in 800 g of demineralized water was introduced

[0039] When the working pressure decreased by 50% with respect to its initial value, i.e. after 290 minutes of reaction, the autoclave was vented and the latex discharged at room temperature

[0040] The obtained latex was diluted with demineralized water to a concentration of 215.2 g of polymer for kg of latex. The latex particles average diameter, measured by DLLS, was 84 nm

20

B) Montmorillonite dispersion

[0041] A montmorillonite dispersion was prepared by using a sodium montmorillonite (MMT), sold as Cloisite Na⁺ (CAS No 1318-93-0) by the Southern Clay company, having the following particle distribution:

25

27.7% > 600 micron,
31.8% in the range 500-250 micron,
36.6% in the range 250-106 micron,
3.9% < 75 micron

30

[0042] 10 g of MMT were dispersed in 200 g of demineralized water under strong mechanical stirring and subsequent ultrasound treatment

[0043] The lamellar inorganic particles have an average thickness of about 2 nm and an average length of 400 nm measured by AFM (Atomic Force Microscopy)

35

C) Preparation of the polymeric composition containing MMT

[0044] In a 2 litre flask 1.5 kg of the PCTFE latex prepared in A) and the MMT dispersion prepared in B) were mixed. After stirring an aqueous mixture containing 19.5% by weight of solid was obtained. Then the solid phase was precipitated by cooling at a temperature of -20°C, separated by filtration and dried at 175°C for 16 hours obtaining a powder

[0045] The powder is constituted by 97% by weight of PCTFE and by 3% by weight of MMT, and has a Melt Flow Index (MI), determined at 265°C with a 10 kg load, equal to 2.7 g/10'

[0046] A compression moulded specimen from said powder has a modulus G' at 150°C as reported in Table 1, and T_{mll} and T_{xxl}, determined with a scanning rate of 40°C/min, as reported in Table 2

45

EXAMPLE 2 (comparative)

[0047] 1.5 kg of the PCTFE latex of Example 1 were precipitated by cooling at temperature of -20°C, the product has been separated and dried at 175°C for 16 hours obtaining a powder.

[0048] The obtained product has a Melt Flow Index (MI), determined at 265°C with a 10 kg load, equal to 41.5 g/10'

[0049] A compression moulded specimen from said powder has a modulus G' at 150°C as reported in Table 1, and T_{mll} and T_{xxl}, determined with a scanning rate of 40°C/min, as reported in Table 2

55

EXAMPLE 3 (comparative)

[0050] 48.5 g of PCTFE powder of Example 2 (comparative) were mixed with 1.5 g of MMT powder, thus obtaining a blend formed by 97% by weight of PCTFE and 3% by weight of MMT

[0051] A compression moulded specimen from said powder has a modulus G' at 150°C as reported in Table 1, and

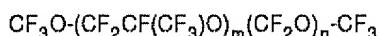
T_{m1} and T_{xx} , determined with a scanning rate of 40°C/min, as reported in Table 2
 [0052] It is possible to notice visually or by optical microscope the presence of MMT particles having the same dimension of the used MMT powder

5 EXAMPLE 4

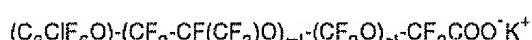
A) Ethylene/chlorotrifluoroethylene latex having molar composition 40/60 (ECTFE)

[0053] In an enamelled autoclave equipped with enamelled baffles and stirrer working at 300 rpm there were introduced in sequence:

- 8.2 l of demineralized water;
- 112.5 g of a microemulsion formed by: 20% by weight of Galden® D02, having formula:



having $m/n = 20$ and average molecular weight of 450; 40% by weight of a surfactant having formula:



having $m1/n1 = 82.7$ and average molecular weight of 527; 40% by weight of demineralized water;

- 25 g of chloroform;
- 4 kg of chlorotrifluoroethylene.

[0054] Then the autoclave was heated to the reaction temperature of 60°C and ethylene was introduced up to a pressure of 21.4 absolute bar. The radical initiator under the form of a solution of 4.8 g of potassium persulphate dissolved in 800 g of demineralized water was then introduced in the autoclave

[0055] The pressure was maintained constant during the whole polymerization by continuously feeding ethylene in the reactor up to a consumption of 230 g. Then the autoclave was vented and the latex discharged at room temperature.

[0056] The obtained latex was diluted with demineralized water to a concentration of 160.1 g of polymer for kg of latex. The latex particles average diameter, determined by DLLS, was 94 nm.

35 B) Laponite dispersion

[0057] A synthetic Hectorite dispersion was prepared by using a hectorite, sold as Laponite RD by the LAPORTE company, having the following particle distribution:

40 0.7% > 600 micron,
 7.3% in the range 500-250 micron,
 52.6% in the range 250-106 micron,
 39.4% < 75 micron

45 [0058] 51 g of Laponite were dispersed in 5.1 kg of demineralized water under strong mechanical stirring obtaining a transparent dispersion

[0059] The lamellar inorganic particles have an average thickness of about 1 nm and an average length of 50 nm measured by AFM (Atomic Force Microscopy)

50 C) Preparation of the polymeric composition containing Laponite

[0060] In a 10 litre flask 5 kg of the ECTFE latex prepared in A) and the Laponite dispersion prepared in B) were mixed

[0061] After stirring an aqueous mixture containing 8.5% by weight of solid was obtained. Then the solid phase was precipitated by cooling at a temperature of -20°C, separated by filtration and dried at 120°C for 16 hours obtaining a powder.

[0062] The powder is constituted by 94% by weight of ECTFE and 6% by weight of Laponite, and has a Melt Flow Index (MI), measured at 210°C with a 10 kg load, equal to 0.36 g/10'

[0063] A compression moulded specimen from said powder has modulus G' values at 23°C, 100°C and 125°C as

reported in Table 3, and T_{mI} and T_{xx} , measured with a scanning rate of 10°C/min, as reported in Table 4

[0064] The mechanical properties measured at 100°C are reported in Table 6

[0065] The X ray analysis on a compression moulded specimen from said powder shows that the dimensions of the inorganic particles are lower than 50 nm

5

EXAMPLE 5

A) Ethylene/chlorotrifluoroethylene latex having molar composition 40/60 (ECTFE)

10 [0066] The ECTFE latex of Example 4 was used

B) Montmorillonite dispersion

[0067] The sodium montmorillonite (MMT) of Example 1 was used

15 [0068] 25 g of MMT were dispersed in 2 5 kg of demineralized water by strong mechanical stirring

[0069] The lamellar inorganic particles have an average thickness of about 2 nm and an average length of 400 nm measured by AFM (Atomic Force Microscopy)

C) preparation of the polymeric composition containing montmorillonite

20 [0070] In a 10 litre flask 5 kg of the ECTFE latex and the MMT dispersion prepared in B) were mixed

[0071] After stirring, an aqueous mixture containing 11% by weight of solid was obtained. Then the solid phase was precipitated by cooling at a temperature of -20°C, separated by filtration and dried at 120°C for 16 hours obtaining a powder

25 [0072] The powder is constituted by 97% by weight of ECTFE and 3% by weight of MMT, and has a Melt Flow Index (MI), measured at 210°C with a 10 kg load, equal to 1 0 g/10'

[0073] A compression moulded specimen from said powder has modulus G' values at 23°C, 100°C and 125°C as reported in Table 3, and T_{mI} and T_{xx} , measured with a scanning rate of 10°C/min, as reported in Table 4

[0074] The mechanical properties measured at 23°C and at 100° are respectively reported in Tables 5 and 6

30

EXAMPLE 6 (comparative)

[0075] 5 kg of the ECTFE latex of Example 4 were precipitated by cooling at a temperature of -20°C, the compound was separated by filtration and dried at 120°C for 16 hours obtaining a powder

35 [0076] The obtained powder has a Melt Flow Index (MI), measured at 210°C with a 10 kg load, equal to 8 2 g/10'

[0077] A compression moulded specimen from said powder has modulus G' values at 23°C, 100°C and 125°C as reported in Table 3, and T_{mI} and T_{xx} , determined with a scanning rate of 10°C/min, as reported in Table 4

[0078] The mechanical properties measured at 23°C and at 100°C are respectively reported in Tables 5 and 6

40 EXAMPLE 7

[0079] The aqueous mixture containing 8 5% by weight of solid obtained in Example 4 C), was used to obtain a film by "spin coating" on a mica surface. The film, after drying, is continuous and uniform

45 EXAMPLE 8 (comparative)

[0080] A powder of an ethylene/chlorotrifluoroethylene copolymer having molar composition 50/50 (ECTFE), having a Melt Flow Index (MI), measured at 275°C with a 2 16 kg load, equal to 7 0 g/10' and a T_{mI} of 240°C, determined with a scanning rate of 10°C/min, was compression moulded obtaining a specimen. The mechanical properties measured at 23°C are reported in Table 7

50 [0081] The powder of the same ECTFE polymer was mixed with mica powder (coated with titanium oxide) IRIODIN® 123 by MERCK, having a particle size in the range 5-25 micron, obtaining a mixture of powders formed by 97% by weight of ECTFE and by 3% of mica, from which a specimen was compression moulded

[0082] The mechanical properties measured at 23°C compared with those of ECTFE not filled with mica, are reported in Table 7

55 [0083] As it is shown in Table 7, the filled ECTFE does not show an improvement of the tensile properties compared with the non-filled ECTFE, except for a slight increase of the elastic modulus. In general a worsening of the tensile properties of the filled ECTFE with respect to the non-filled ECTFE is noticed

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Table 1

"Storage Modulus" G' (MPa)	Example 1	Example 2 (comp)	Example 3 (comp)
at 150°C	200	80	80

Table 2

	Example 1	Example 2 (comp)	Example 3 (comp)
T _{ml} (°C)	213 8	215 0 0	215 0
T _{xx} (°C)	188 0	173 9	176 9

Table 3

"Storage Modulus" G' (MPa)	Example 4	Example 5	Example 6 (comp)
at 23°C	691	741	533
at 100°C	21 6	19 3	10 0
at 125°C	13 9	13 0	6 8

Table 4

	Example 4	Example 5	Example 6 (comp)
T _{ml} (°C)	157 4	158 3 3	160 6
T _{xx} (°C)	141 0	144 2	141 0

Tabella 5

Mechanical properties at 23°C	Example 5	Example 6 (comp)
Elastic Modulus (MPa)	1413	1074
Yield stress (MPa)	27 4	24 0
Elongation at break (%)	269	270

Table 6

Mechanical properties at 100°C	Example 4	Example 5	Example 6 (comp)
Elastic Modulus (MPa)	43	29	16
Yield stress (MPa)	2 9	2 7	1 9
Stress at break (MPa)	3 0	2 7	2 7
Elongation at break (%)	363	399	763

Table 7

Mechanical properties at 100°C	Example 8 (comp)	
	ECTFE + 3% mica	ECTFE
Elastic modulus (MPa)	1598	1480
Yield stress (MPa)	27	32
Stress at break (MPa)	44	55
Elongation at break (%)	178	240

Claims

1. A polymeric composition comprising:

- a) from 90 to 99.9% by weight of a fluoropolymer; and homogeneously dispersed
- b) from 0.1 to 10% by weight of lamellar inorganic particles having at least one dimension lower than 100 nm.

2. A composition according to claim 1, wherein the fluoropolymer a) is selected from the group formed by polymers or semicrystalline thermoplastic copolymers having a second melting temperature lower than 310°C

3. A composition according to claims 1-2, wherein the fluoropolymer is a chlorotrifluoroethylene homopolymer (PCTFE) or a copolymer with fluorinated or acrylic monomers, or a copolymer of ethylene with CTFE and/or TFE, optionally containing fluorinated or acrylic monomers

4. A composition according to claims 1-3, wherein the lamellar inorganic particles b) are preferably formed by silicates, more preferably aluminum-silicates and/or magnesium-silicates containing other metals such as sodium, potassium, iron or lithium

5. A composition according to claims 1-4, wherein the lamellar inorganic particles have at least one dimension lower than 50 nm, more preferably lower than 10 nm

6. A composition according to claims 1-5, wherein the polymeric composition preferably contains from 0.3 to 6% by weight of lamellar inorganic particles b)

7. A preparation process of the composition according to claims 1-6, comprising:

- 1) preparation of an aqueous fluoropolymer latex having a concentration between 5 and 60% by weight, preferably between 15 and 30% by weight of fluoropolymer;
- 2) preparation of an aqueous dispersion of lamellar inorganic particles having a thickness lower than 100 nm, preferably lower than 50 nm, more preferably lower than 10, and the other two dimensions lower than 10,000 nm, preferably lower than 2,000, more preferably lower than 500 nm, by mixing the inorganic component having a layered lamellar morphology with water until obtaining a concentration comprised between 0.1 and 10% by weight, preferably between 0.5 and 2%, under stirring (a strong mechanical stirring and/or an ultrasound treatment), at a temperature in the range 20°C-300°C, preferably 50°C-100°C;
- 3) mixing, under stirring, of the latex obtained in 1) with the aqueous dispersion obtained in 2);
- 4) precipitation of the solid phase from the aqueous mixture obtained in 3) by cooling at temperatures lower than 0°C or by increasing the ionic force or by pH variations;
- 5) separation and drying at temperatures from 50°C to 250°C of the solid phase obtained in 4)

In step 2) the stirring is preferably a strong mechanical stirring and/or an ultrasound treatment.

8. A process according to claim 7, wherein when the concentration of the latex prepared in 1) is lower than 30% the inorganic component having a layered lamellar morphology is directly added to said latex

9. A process according to claims 7-8, wherein the latex fluoropolymers particles have dimensions comprised between 20 and 300 nm, preferably between 50 and 150 nm

10. Shaped articles, such sheets, pipes, films obtainable by compression moulding or extrusion of the compositions according to claims 1-6

11. Aqueous mixture comprising from 5% to 90% by weight of:

5 I) fluoropolymer a) particles according to claims 1-6, having dimensions in the range 20-300 nm; and
II) lamellar inorganic particles b) according to claims 1-6, having at least one dimension lower than 100 nm,

10 wherein the ratio by weight between the fluoropolymer a) and the lamellar inorganic component is in the range 1-1,000

12. Use of the aqueous mixture according to claim 11, to prepare films or coatings

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EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.7)						
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim							
D,X	WO 98 10012 A (RAYCHEM CORP) 12 March 1998 (1998-03-12) * page 11, line 9 - line 15; claims; examples 2-4 *	1-6,10	C08K7/00 C08L27/12						
X	WO 99 07781 A (DU PONT) 18 February 1999 (1999-02-18) * claims; examples *	1-6,10							
X	US 5 840 796 A (BADESHA SANTOKH S ET AL) 24 November 1998 (1998-11-24) * claims; examples *	1-6,10							
X	US 5 310 775 A (SIBILIA JOHN P ET AL) 10 May 1994 (1994-05-10) * claims; examples *	1-6,10							
X	US 6 218 000 B1 (RUDOLF CHRISTIANE ET AL) 17 April 2001 (2001-04-17) * column 4, line 39 - line 45 * * column 6, line 63 - column 7, line 28; claims; examples 7,9,10,12 *	7-9,11, 12							
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)						
			C08L C08K						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 33%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>27 November 2003</td> <td>DE LOS ARCOS, E</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	27 November 2003	DE LOS ARCOS, E
Place of search	Date of completion of the search	Examiner							
THE HAGUE	27 November 2003	DE LOS ARCOS, E							
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document							
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document									

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 03 01 1987

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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27-11-2003

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
WO 9810012	A	12-03-1998	US EP JP TW WO	5962553 A 0927223 A1 2001523278 T 409136 B 9810012 A1	05-10-1999 07-07-1999 20-11-2001 21-10-2000 12-03-1998
WO 9907781	A	18-02-1999	EP JP WO	1002010 A1 2001512768 T 9907781 A1	24-05-2000 28-08-2001 18-02-1999
US 5840796	A	24-11-1998		NONE	
US 5310775	A	10-05-1994		NONE	
US 6218000	B1	17-04-2001	DE AT AU AU BG CA CN DE DE DE DE WO EP EP ES JP JP PL WD US	19544912 A1 236210 T 1032797 A 6687396 A 102398 A 2233695 A1 1203610 A ,B 59610317 D1 69617707 D1 69617707 T2 9720881 A1 0850265 A1 0951500 A1 2164909 T3 11515036 T 11501973 T 327032 A1 9706206 A1 5814405 A	05-06-1997 15-04-2003 27-06-1997 05-03-1997 30-12-1998 20-02-1997 30-12-1998 08-05-2003 17-01-2002 08-05-2002 12-06-1997 01-07-1998 27-10-1999 01-03-2002 21-12-1999 16-02-1999 09-11-1998 20-02-1997 29-09-1998